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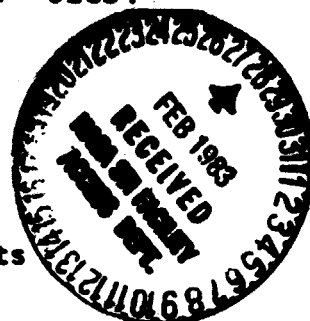
FINAL REPORT

from the University of Massachusetts

JPL CONTRACT NO. 955531

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It was the objective of this work to assist the Encapsulation Task Force of the Flat-Plate Solar Array Project at the Jet Propulsion Laboratory (JPL) to devise polymeric materials that are stable enough to use outdoors without changes in excess of 20 years. Our particular objective was to synthesize new and effective ultraviolet stabilizers for plastic materials, to prepare polymerizable ultraviolet stabilizers, particularly of the 2(2-hydroxyphenyl)2H-benzotriazole family, to demonstrate their polymerization, copolymerization and grafting onto other polymers, to devise new effective ultraviolet stabilizing systems and to assist JPL in their evaluation of these materials from the photophysical point of view.

This work has been carried out since September, 1979, and was principally done by the following coworkers: Witold Pradelok, Zohar Nir, Eberhard Borsig and Shen-Jun Li. Benefits for the project supported by JPL were obtained from work that has been going on for many years and concurrently in our research group on polymerizable ultraviolet stabilizers and polymerizable antioxidants (D. Tirrell, D. Bailey, M. Kitayama, Y. Sumida, S. Yoshida, and P. Grosso).

The first successfully concluded project for JPL was the preparation of 2(2-hydroxy-5-vinylphenyl)2H-benzotriazole (2H5V) and 2(2-hydroxy-5-isopropenylphenyl)2H-benzotriazole (2H5P). 2H5V had been synthesized before by S. Yoshida in a six-step reaction consisting of the condensation of o-nitrobenzenediazonium chloride with p-ethylphenol; this reaction gave an azo compound which was reduced by zinc and sodium hydroxide to 2(2-hydroxy-5-ethylphenyl)2H-benzotriazole and was acetylated, brominated, dehydrobrominated and finally hydrolyzed to 2H5V.

The achievement in the first six months of the contract was to prepare about 350 grams of 2H5V for the use of JPL. This material has been sent, in stabilized form (with picric acid to avoid polymerization) to JPL. 2H5V readily homopolymerized and also copolymerized with normal resonance stabilized monomers such as styrene, methyl methacrylate and n-butyl acrylate.

2H5V was then synthesized and a new synthesis of 2H5V was devised by condensation of 4-hydroxybenzophenone with o-nitrobenzenediazonium chloride. The key intermediate for the final synthetic steps is 2(2-acetoxy-5-acetylphenyl)2H-benzotriazole which could be reduced with sodium borohydride, dehydrated and hydrolyzed to 2H5V or allowed to react with methyl Grignard reagent, dehydrated and hydrolyzed to 2H5P. Adequate amounts of this compound (over 50 grams) were prepared for various homo- and copolymerization, grafting studies and a portion was sent to JPL for evaluation. 2H5V is quite different in reactivity as compared to 2H5P; it does not homopolymerize and is stable without additional stabilizer added to prevent polymerization. It is (because of its tertiary

carbon atom in the polymeric form) also expected to be more photostable.

Many routes (at least 10) were evaluated for the most efficient or more direct route to 2H5P, none of which resulted in the synthesis of 2H5P.

2H5V and 2H5P copolymerized with such monomers as styrene, methyl methacrylate, and n-butyl methacrylate. The reactivity ratios of these copolymerizations were determined and it was shown that 2H5V is very readily incorporated into all of these copolymers. The 2H5P r value is near 0 indicating alternating tendency for this comonomer; not surprising since this is an α -methylstyrene derivative.

2H5V and 2H5P were also incorporated into other polymer systems. 2H5V very readily grafted in solution in chlorobenzene at about 150°C with di-tertiary butyl peroxide to form graft polymers with atactic polypropylene, ethylene/vinyl acetate copolymers, ethylene/propylene copolymer, poly(methyl methacrylate) and poly(n-butyl acrylate). It was also shown that 2H5V is readily grafted under much milder conditions onto cis-1,4 polybutadiene and 1,2-polybutadiene at good grafting efficiency and without crosslinking. 2H5V and 2H5P were also incorporated into ethylene/vinyl acetate copolymers under grafting/crosslinking conditions.

Unsaturated polyesters were copolymerized in the presence of 2H5V and 2H5P in styrene solution to form unsaturated polyester resins now photostabilized with our polymerizable UV absorbers. This work is done in cooperation with Professor Ranby in Sweden; by ESCA measurements, he is determining the actual placements of the stabilizer on the surface of the stabilized film. He is also studying the effect of singlet oxygen (1O_2) and various accelerated aging

conditions on such permanently photostabilized unsaturated polyester resins.

In our early work on polymerizable stabilizers of the benzotriazole family we had also been trying to synthesize 2(2-hydroxy-4-vinylphenyl)2H-benzotriazole and 2(2-hydroxy-3-vinylphenyl)2H-benzotriazole. All our efforts to date failed and we have abandoned these objectives. In all cases parasubstitution, rather than orthosubstitution occurred which gave the wrong (4-) isomer, non-effective as UV stabilizer. Dr. S. Yoshida, however, was successful in synthesizing the 2(2-hydroxy-5-methylphenyl)2H-5'-vinyl-benzotriazole. It behaves similarly to 2H5V, can be polymerized and copolymerized with the standard monomers but does not seem to offer any advantages over 2H5V or 2H5P.

On a separate project, not supported by JPL, we have also studied the synthesis of polymerizable antioxidants particularly 4-vinyl-2,6-tertiary butylphenol and 4-isopropenyl-2,6-tertiary butylphenol. They can be readily polymerized directly with styrene and methyl methacrylate in bulk and in solution but more importantly they could be copolymerized in emulsion with butadiene and isoprene. These two polymerizable antioxidants could be available whenever needed for our project of long-term stabilization of polymeric materials, long-term stabilizations using non-leachable, non-volatilizable stabilizers.

More recently we have emphasized our thrust in the synthesis of new and much more effective stabilizing systems. These systems are still based on the 2(2-hydroxyphenyl)2H-benzotriazole and 2-hydroxybenzophenone chromophors.

We have synthesized three new systems of UV absorbing chromophors some of which we have started to convert into polymerizable monomers. The objective of the initial work, however, was to synthesize and identify these new systems in

order to make them available for JPL to study their effectiveness to improve the aging of polymeric material and to evaluate their photophysical behavior.

We have found that resorcinol, 1,3-dihydroxybenzene, not only forms a monosubstitution product, when allowed to react with o-nitrobenzenediazonium chloride followed by reductive cyclization (called benzotriazolization), but more importantly a disubstituted product was readily obtained. With phloroglucinol, o-nitrobenzenediazonium chloride, after condensation and reductive cyclization, not only gave a disubstituted product but also a tribenzotriazolized material. These three new compounds show surprisingly high extinction coefficients, three times as high as the normal monosubstituted benzotriazole derivatives but also a broad absorption from 250 nm to 360 nm.

2,4-Dihydroxybenzophenone and 2,4-dihydroxyacetophenone (which are themselves effective ultraviolet stabilizers) have been used as starting material for benzotriazolization and indeed dibenzotriazolized products have been obtained in both cases. The absorption spectrum of these compounds show extinction coefficients lower than those of the di- and tribenzotriazolized resorcinols and benzophenones (only two-thirds of the extinction coefficient) however, they show an additional strong band between 260 and 300 nm. It is interesting that in the case of the dibenzotriazolized 2,4-dihydroxybenzophenone we have now a system which has both of the most important ultraviolet stabilizing groups in one molecule, the 2(2-hydroxyphenyl)2H-benzotriazole and the 2-hydroxybenzophenone chromophor.

The product from the acetophenone derivative is also planned to be used as a starting material for the synthesis of styrene and ~~of~~-methylstyrene derivatives of these highly substituted benzotriazole containing systems therefore giving new polymerizable ultraviolet stabilizer systems.

The benzotriazolization of phloroglucinol had initially yielded only the di- and trisubstituted product as the condensation of o-nitrobenzenediazonium chloride with phloroglucinol were always carried out in strongly basic solutions. It is known that phloroglucinol is very reactive and the reason for it is that it exists, as we have shown very recently, to a substantial amount in the keto form which is apparently undergoing the condensation reaction. By carrying out the condensation in near neutral aqueous/alcoholic solutions we were able to prepare the azo compound which, after reductive cyclization, produced monosubstituted phloroglucinol, namely 2(2,4,6-trihydroxyphenyl)2H-benzotriazole.

Some initial work has been done to react these new stabilizers with more than one benzotriazol units in the molecule with acryl and methacryl chloride in order to provide polymerizable methacrylic and acrylic esters of ultraviolet absorbers. Some of the materials will also be used either directly or in the appropriately modified form for incorporation in polyesters and polycarbonates.

In conclusion, we have successfully prepared polymerizable ultraviolet stabilizers which can be incorporated into polymers by copolymerization and grafting. We have also prepared new classes of ultraviolet stabilizers which have high extinction coefficient and are effective over a broad spectrum of ultraviolet absorption. This work will produce new and more efficient stabilizers which could be used either by themselves or when transformed into polymerizable ultraviolet stabilizer would be incorporated into polymers by copolymerization or grafting. We are convinced that these new discoveries and developments on ultraviolet absorbers will provide further advances in extending the lifetime of polymeric materials.

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